

5009 A

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 745 660 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

04.12.1996 Bulletin 1996/49

(51) Int. Cl.⁶: C10G 45/08, B01J 37/08

(21) Application number: 95113698.5

(22) Date of filing: 31.08.1995

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 02.06.1995 JP 158817/95

(71) Applicant: MITSUBISHI OIL CO., LTD.
Minato-ku Tokyo (JP)

(72) Inventors:
• Sadakane, Osamu
Ota-ku, Tokyo (JP)

• Sasaki, Yoichi
Ota-ku, Tokyo (JP)
• Ohnishi, Ryozi
Kitasoma-gun, Ibaragi (JP)

(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem.
et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
81925 München (DE)

(54) **Desulphurization method for catalytically cracked gasoline**

(57) A desulfurization method for catalytically cracked gasoline includes subjecting catalytically cracked gasoline containing sulfur compounds to a hydrodesulfurization treatment using a catalyst having deposited on the surface thereof coke in an amount of from about 3 to about 10% by weight of the catalyst. Preferably, the coke has an atomic ratio of carbon to hydrogen of not higher than 0.7.

EP 0 745 660 A1

fin components are hydrogenated to lower the octane value but also the control of the reaction temperature is difficult because of the heat generated by the hydrogenation. Also, the reaction proceeds locally to increase the temperature, whereby there is a possibility that the catalyst is quickly deteriorated. Catalytically cracked gasoline usually contains about 30% by volume olefin components, and when these olefin components are hydrogenated, the temperature increases greatly and reaches 100°C at the highest. For preventing the large temperature increase, it is necessary to gradually pass catalytically cracked gasoline and increase the temperature while applying a heat removing and cooling counterplan such as hydrogen quenching, etc.

Since coke is also deposited by the desulfurization reaction of catalytically cracked gasoline, when the deposited amount of coke reaches about 3% by weight of the catalyst, the hydrogenation reaction is restrained. However, not only the temperature management is difficult until reaching a stabilized stage but also even a danger of causing a run-away reaction follows. Also, during the period before the stabilized stage, the hydrogenation ratio of olefin becomes high and the octane value becomes low, whereby expressly desulfurized gasoline cannot be utilized as a gasoline stock and must be diverted as a petrochemical naphtha having a low addition value.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a desulfurization treatment method for catalytically cracked gasoline by contacting catalytically cracked gasoline containing sulfur compounds and olefin components with a catalyst, wherein the hydrogenating exothermic reaction of olefin components is restrained from the beginning of the initiation of the reaction, lowering of the octane value is less, and the stabilized reaction can be carried out.

As the result of various investigations for solving the foregoing theme, the inventors have achieved the epoch-making present invention of subjecting catalytically cracked gasoline containing sulfur compounds to a hydro-desulfurization treatment using a catalyst having deposited on the surface thereof coke in an amount of from about 3 to about 10% by weight of the catalyst. In one embodiment, the present invention involves subjecting catalytically cracked gasoline containing sulfur compounds and olefin components to a hydrodesulfurization treatment, which comprises carrying out the reaction using a coke-modified catalyst having deposited on the surface thereof coke in an amount of from about 3 to about 10% by weight of the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

When coke is deposited on the surface of a catalyst, both the desulfurizing activity and the hydrogenating activity of olefins are lowered, but in this case, since

the lowering extent of the activity is larger in the hydrogenating activity, when the reaction is carried out at the same desulfurization ratio, the hydrogenation ratio of olefins is restrained, and the desulfurization proceeds selectively. Also, since the hydrogenation reaction, which is an exothermic reaction, is restrained, a stabilized desulfurization can be operated. When the amount of coke being deposited on the surface of the catalyst is from about 3 to about 10% by weight, which is the range defined in this invention, a high desulfurization ratio and an excellent selectivity can be attained.

The amount of coke to be deposited can be selected in the range of from about 3 to about 10% by weight as described above. For maximally restraining the hydrogenating activity of olefins and minimizing lowering of the octane value, the deposition amount of coke may be increased, and when a high desulfurization faculty is desired while allowing lowering of the octane value a little, the deposition amount of coke may be decreased. If the deposition amount of coke is less than about 3% by weight, the hydrogenating activity of olefins is not sufficiently restrained, whereby the feature of the present invention is difficult to be obtained, while if the deposition amount of coke is over about 10% by weight, the influence on the life of the catalyst becomes large.

As to the property of coke which is used for modifying the catalyst in this invention, it is preferred that the atomic ratio of carbon to hydrogen is not higher than 0.7. The coke wherein the atomic ratio of carbon to hydrogen is not higher than 0.7 is a so-called soft coke, and in the case of using such a coke, since the pores and the active points of the catalyst are incompletely covered by the coke, sulfur compounds in the gaseous state easily reach the active points and are desulfurized. A coke wherein the atomic ratio of carbon to hydrogen is higher than 0.7 is a strong coke clogging the pores and the active points of the catalyst, and in the case of using such a coke, the desulfurization activity of the catalyst is greatly lowered.

As a modification method with coke, any desired method may be used, but a method of depositing coke by contacting hydrocarbons, etc., with the catalyst is generally used. In this case, it is preferred that the hydrocarbons be brought into contact with the catalyst, and the conditions of contacting the hydrocarbons with the catalyst are selected such that coke having an atomic ratio of carbon to hydrogen not higher than 0.7 is deposited on the surface of the catalyst. For example, there is a method of contacting hydrocarbons having a ratio of olefin components in the composition of not more than about 10% by volume, a content of dienes of not more than 0.1% by volume, a content of bicyclic aromatics of not more than about 5% volume, and a content of tricyclic or more aromatics of not more than 1% by volume and having a boiling point of not higher than about 300°C with the catalyst together with hydrogen. Furthermore, it is more preferred to use hydrocarbons not containing olefin components, dienes, and bicyclic or more aromatics. This is because these components

value, which is an important feature of the present invention.

The present invention is explained in more detail by the following examples, which should not be construed as limiting the present invention in any way. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

Example 1

In each of two fixed bed, ascending, cocurrent systems, a small-sized reaction apparatus was packed with 60 ml of a 1/16-inch, extrusion-molded, commercially available catalyst composed of an alumina carrier carrying thereon 4% by weight CoO and 15% by weight MoO₃.

Then, a straight run gasoline fraction of a temperature of from 30°C to 150°C added with 5% by weight dimethyl disulfide was used for pre-sulfurization in each of the two reaction apparatus for 5 hours at a temperature of 300°C, a pressure of 15 kg/cm², an LHSV of 2 per hour, and a hydrogen/oil ratio of 500 scf/bbl.

After finishing the pre-sulfurization, the temperature of each reaction apparatus was increased to 330°C, and a straight run kerosene (olefin content: not detected, dienes: not detected, bicyclic or more aromatics: 0.5% by volume) having a boiling point range of from 150°C to 250°C was passed through each reaction apparatus for 24 hours at an LHSV of 5 per hour, a hydrogen partial pressure of 15 kg/cm², and a hydrogen/oil ratio of 500 scf/bbl. When the catalyst was taken out from one of the reaction apparatus and analyzed, the deposited amount of coke was 3.9% by weight, and the atomic ratio of carbon to hydrogen was 0.53.

In another reaction apparatus, catalytically cracked gasoline of 80°C to 220°C fractions obtained by catalytically cracking a stock oil containing an atmospheric residual oil was successively subjected to a desulfurization reaction test as catalytically cracked gasoline. The density was 0.779 g/cm³ at 15°C, the sulfur content was 220 ppm by weight, the olefin content was 32% by volume, and the research octane number was 87.1.

For the reaction conditions, the temperature was 250°C, the hydrogen partial pressure was 12 kg/cm², the LHSV was 7 per hour, and the hydrogen/oil ratio was 2000 scf/bbl. As a result thereof, hydrodesulfurization treated catalytically cracked gasoline having a sulfur content of 63 ppm by weight, an olefin content of 29% by volume, and a research octane number of 86.0 was obtained.

Example 2

Using the two reaction apparatus and the catalyst as used in Example 1, pre-sulfurization was carried out in the same manner as in Example 1.

After the pre-sulfurization was over, the temperature of each reaction apparatus was increased to 350°C, and a straight run heavy gasoline fraction (olefin

content: not detected, dienes: not detected, bicyclic or more aromatics: 0.1% by volume) having a boiling point range of from 120°C to 230°C was passed through each reaction apparatus for 72 hours at an LHSV of 5 per hour, a pressure of 15 kg/cm², and a hydrogen/oil ratio of 500 scf/bbl.

When the catalyst was taken out from one of the reaction apparatus and analyzed, the deposited amount of coke was 7.3% by weight, and the atomic ratio of carbon to hydrogen was 0.58.

In another reaction apparatus, the catalytically cracked gasoline as used in Example 1 was subjected to a desulfurization reaction test under the same conditions as in Example 1. As a result thereof, hydrodesulfurization treated catalytically cracked gasoline having a sulfur content of 72 ppm by weight, an olefin content of 31% by volume, and a research octane number of 86.9 was obtained.

Example 3

Using the two reaction apparatus and the catalyst as used in Example 1, pre-sulfurization was carried out in the same manner as in Example 1.

After the pre-sulfurization was over, a mixture oil of 20 parts by weight of the catalytically cracked gasoline of 80°C to 220°C fractions and 80 parts by weight of the straight run kerosene fractions having a boiling point range of about 150°C to 250°C as used in Example 1 was passed through each reaction apparatus for 72 hours at a temperature of 300°C, an LHSV of 5 per hour, a pressure of 15 kg/cm², and a hydrogen/oil ratio of 500 scf/bbl.

When the catalyst was taken out from one of the reaction apparatus and analyzed, the deposited amount of coke was 5.8% by weight, and the atomic ratio of carbon/hydrogen was 0.55.

Then, using the catalytically cracked gasoline as used in Example 1, the desulfurization reaction test was carried out using another reaction apparatus under the same conditions as in Example 1. As a result thereof, hydrodesulfurization treated catalytically cracked gasoline having a sulfur content of 65 ppm by weight, an olefin content of 30% by volume, and a research octane number of 86.7 was obtained.

Example 4

When coke of a hydrodesulfurized catalyst (a 1/16-inch, extrusion-molded, commercially available catalyst composed of an alumina carrier carrying 4.5% by weight CoO and 17% by weight MoO₃) used for the desulfurization of gas oils for 2 years was analyzed, the deposited amount of the coke was 8.6% by weight, and the atomic ratio of carbon to hydrogen was 0.74. Then, 60 ml of the catalyst was packed in the reaction apparatus used in Example 1, and using the catalytically cracked gasoline as used in Example 1, the desulfurization reaction test was carried out under the same condi-

hydrogen partial pressure of from about 5 to about 15 kg/cm², a hydrogen/oil ratio of from about 500 to about 3000 scf/bbl, and a liquid hourly space velocity of from about 2 to about 10 per hour.

7. The desulfurization method for catalytically cracked gasoline described in claim 1, wherein the catalyst contains cobalt and molybdenum. 5
8. The desulfurization method for catalytically cracked gasoline described in claim 1, wherein the catalyst contains nickel, cobalt and molybdenum. 10
9. The desulfurization method for catalytically cracked gasoline described in claim 2, wherein the catalyst contains cobalt and molybdenum. 15
10. The desulfurization method for catalytically cracked gasoline described in claim 2, wherein the catalyst contains nickel, cobalt and molybdenum. 20
11. The desulfurization method for catalytically cracked gasoline described in claim 3, wherein the catalyst contains cobalt and molybdenum. 25
12. The desulfurization method for catalytically cracked gasoline described in claim 3, wherein the catalyst contains nickel, cobalt and molybdenum.
13. The desulfurization method for catalytically cracked gasoline described in claim 3, wherein the reaction apparatus is a fixed bed system. 30
14. The desulfurization method for catalytically cracked gasoline described in claim 4, wherein the catalyst contains cobalt and molybdenum. 35
15. The desulfurization method for catalytically cracked gasoline described in claim 4, wherein the catalyst contains nickel, cobalt and molybdenum. 40
16. The desulfurization method for catalytically cracked gasoline described in claim 4, wherein the reaction apparatus is a fixed bed system. 45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 3698

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 582 403 (TEXACO) * claims 1,2,7,8,13 * * page 3, line 52 - line 55 * * page 5, line 21 - line 26 * ---	1,3,7, 11,13	C10G45/08 B01J37/08
A	EP-A-0 541 994 (IDEMITSU KOSAN CO LTD) * claims 12,8,9,10 * * page 1, line 22 - line 30 * -----	1,7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C10G B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 6 September 1996	Examiner De Herdt, O
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03.92) (P0/C01)